

the curve fitting stress/strain relation $\sigma = \sigma_0 \epsilon^n$. Despite the low strength of the alloy used in the present experiments, ρ/σ_0 lies between 4 and $5 \times 10^{-6} \text{ sec}^2 \text{ m}^{-2}$ which compares well with steel and aluminium armour [5] because of the low density of magnesium. Nevertheless this assessment method assumed a ductile failure mode of the material and the present alloy does not achieve its full potential because of the discing-type failure.

There are two possible methods of overcoming the deleterious effects of discing. One approach has been to change the crystal structure by suitable alloying additions, as has been done with magnesium–lithium alloys [1]. The other technique is to hold the back of the target so that the projectile must deform the full thickness of the magnesium in order to penetrate. This can be achieved using a ductile back-up plate of sufficient stiffness that bending is limited during penetration [6]. The bending requirement means that the back-up plate must have a thickness of the order of the projectile diameter. In such a case, the penetration resistance and weight penalties must be assessed with the composite structure in mind.

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Non-stoichiometry of $(\text{La}_{0.8}\text{Ca}_{0.2})\text{MnO}_{3+y}$

Several investigations of the crystal structure of the magnetic oxide $(\text{La}_{0.8}\text{Ca}_{0.2})\text{MnO}_3$ have been reported [1–6]. The present study is of the non-stoichiometry and the lattice constants of $(\text{La}_{0.8}\text{Ca}_{0.2})\text{MnO}_{3+y}$ (y : parameter of the non-stoichiometry).

The factors determining y in the preparation of the material are temperature and oxygen partial pressure and, therefore, the oxygen partial pressure was controlled with $\text{CO}_2\text{--H}_2$ or $\text{CO}_2\text{--O}_2$ mixtures [7–9]. In order to measure the relative value of y , a thermal balance of which the sensitivity is 0.1 mg was employed, and a stabilized ZrO_2 cell was used to take measurements of the oxygen partial pressures. Here, p_{O_2} (oxygen partial pressure) can be written as

(a) $\text{CO}_2\text{--H}_2$ mixture:

$$p_{\text{O}_2}(\text{MPa}) = 0.10199 \times 10^{-11}$$

$$\times \{r - 1 + [(r - 1)^2 + 4r/2.456]^{1/2}\}^2/4 \quad (1)$$

at 1473 K, where $r = p_{\text{CO}_2}(\text{i})/p_{\text{H}_2}(\text{i})$: the ratio of the initial partial pressures of CO_2 and H_2 at room temperature, and $\text{MPa} = 10^6 \text{ Nm}^{-2} = 9.869233 \text{ atm}$;

(b) $\text{CO}_2\text{--O}_2$ mixture:

$$p_{\text{O}_2}(\text{MPa}) = 0.101325(2r + f)/(2 + 2r + f), \quad (2)$$

$$f = 1.0033(1 - f)[(2 + 2r + f)/(2r + f)]^{1/2}. \quad (3)$$

Equation 3 is iterated using $f = 0$ as the initial value. The result of the iteration is substituted into Equation 2 and then p_{O_2} is obtained. When $r > 0.01$ this result is well approximated by

$$p_{O_2}(\text{MPa}) = 0.101325r/(1+r), \quad (4)$$

at 1473 K.

p_{O_2} was then measured using a stabilized ZrO_2 cell which produces an electric voltage in response to the oxygen pressure difference between both sides of the cell. From the Nernst equation

$$E(\text{volt}) = 4.96025 \times 10^{-5} T(K) \times \log[p_{O_2}(1)/p_{O_2}(2)], \quad (5)$$

where $p_{O_2}(1)$ and $p_{O_2}(2)$ are p_{O_2} of the sides (1) and (2) of the cell. The pure oxygen at atmospheric pressure flows in side (2) of the cell as the standard partial pressure of oxygen.

The reagents used were La_2O_3 (99.997%, Halewood Chemicals Ltd), MnO_2 (99.999%, Johnson Matthey Chemicals Ltd) and $CaCO_3$ (99.999%, specpure, Johnson Matthey Chemicals Ltd). When MnO_2 is heated in air at 1372 to 1808 K, it changes into Mn_3O_4 which is very close to the stoichiometric composition [10]. La_2O_3 was heated at about 1800 K for 1 h in air. Mn_3O_4 , La_2O_3 and $CaCO_3$ were mixed under acetone for several hours, and heated at 1300 K in air in an alumina crucible with an alumina lid to prevent losing the sample by degassing of $CaCO_3$. The heated mixture changed to the perovskite-type compounds. The compounds obtained were pulverized with an agate mortar and pestle under acetone for several hours and dried at about 383 K. The samples were then maintained at 1473 K for about 24 h to reach equilibrium with a certain p_{O_2} . At this temperature, the metal ions do not sublime as was seen from the fact that the weight of the sample remained constant

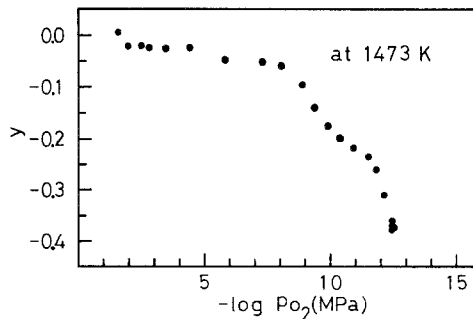


Figure 1 The relation between the parameter of the non-stoichiometry y and the oxygen partial pressure obtained by the thermal balance at 1473 K. The sample decomposes at $10^{-12.56}$ (MPa) at 1473 K.

within experimental error for 10 days at 1473 K after the initial change in weight. The experiment indicates that the metal ions sublime at 1523 K. To obtain the absolute value of y from the relative value of y obtained by a thermal balance, it is necessary to measure the weight of a standard point. As the standard point, the weight after decomposition of $(La_{0.8}Ca_{0.2})MnO_3$ into La_2O_3 , CaO and MnO at $10^{-12.56}$ (MPa), 1473 K was used. At this condition the value [11] of O/Mn of MnO is very close to 1. When the specimens for measuring the lattice constants were prepared, they were quickly quenched to room temperature after maintaining them at the desired conditions for about 24 h.

After the runs the samples were analysed by X-ray diffraction with nickel-filtered copper radiation using Si powder as internal standard.

The relation between $-\log p_{O_2}$ (MPa) and y is shown in Fig. 1. The decomposition of

TABLE I d -values for the samples which could not be indexed

$y = -0.22(0)$	$y = -0.26(8)$	$y = -0.30(8)$	$y = -0.37$
3.9673	3.9726	3.9621	3.9885
3.8503	3.8519	3.7139	3.7354
3.5268	3.7047	3.5254	2.8805
2.8412	3.5337	3.1695	2.7650
2.7642	3.1817	2.8607	2.5982
2.6688	2.8580	2.7633	2.2515
2.2878	2.7658	2.7321	2.1401
2.2478	2.7248	2.2461	2.0892
2.0010	2.878	2.1238	1.9537
1.9123	2.2488	2.0846	1.6871
1.5971	2.1238	2.0705	1.6145
	1.9868	1.9848	1.5946
	1.9309	1.9449	
		1.9255	

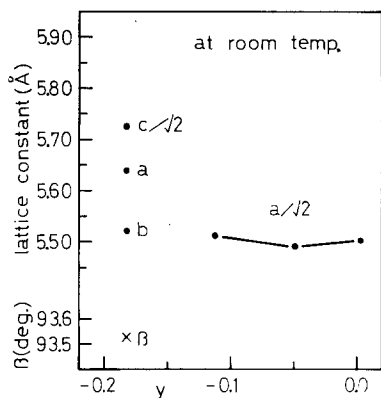


Figure 2 The relation between the lattice constants and y .

$(\text{La}_{0.8}\text{Ca}_{0.2})\text{MnO}_3$ occurred at 10^{-12} MPa and 1473 K. Generally, y is a function of the temperature even if the oxygen pressure is fixed; therefore, the samples for measuring the lattice constants were quenched after being maintained at high temperature. The value of y at 1473 K in air is close to 0. At 10^{-12} (MPa) about 10% of the oxygen ions are deficient, which means that the number of the nearest neighbour oxygen vacancies around an Mn ion is about 0.6 and the number of them around an La(Ca) ion is about 1.2.

The results of X-ray powder diffraction studies are shown in Table I and Fig. 2. The unit cells are shown in Fig. 3. For the cubic lattice, eight unit formulae are contained per unit cell. For the monoclinic lattice the, four unit formulae are contained per unit cell, and a_0 denotes the lattice constant of the usual perovskite-type crystal

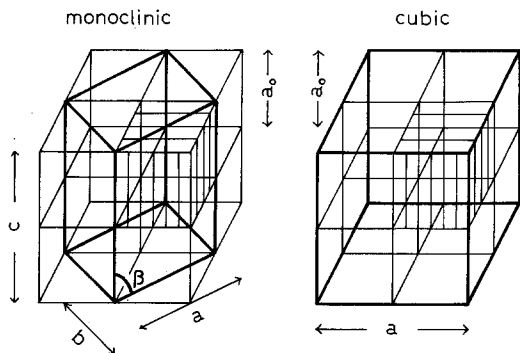


Figure 3 The unit cells of the monoclinic lattice and the cubic lattice. a_0 denotes the lattice constant of the usual perovskite-type crystal.

containing one unit formula per unit cell. The lattices are cubic for $\sim -0.15 < y < 0.00$ and monoclinic for $y = -0.18$ (2). Although the distortion of octahedrons of six oxygens cannot be calculated from the lattice parameters in this case, it seems that the distortions by the Jahn–Teller effect arising from Mn^{3+} ions occur when the cells are cubic. This effect may be the origin for the cubic unit cell to contain eight unit formulae. The lattice constants for $y < \sim -0.2$ could not be determined (Table I).

No recognizable changes were observed in the d -values for the sample ($y = -0.37$) immediately after preparation and for that kept in a plastic vessel for 1 year.

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